(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 246 418 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
22.11.2017 Bulletin 2017/47

(21) Application number: **15877751.6**

(22) Date of filing: **03.12.2015**

(51) Int Cl.:
C21D 8/10 (2006.01) ***C21D 9/08*** (2006.01)
C22C 38/00 (2006.01) ***C22C 38/58*** (2006.01)
C21D 6/00 (2006.01) ***C22C 38/02*** (2006.01)
C22C 38/04 (2006.01) ***C22C 38/06*** (2006.01)
C22C 38/40 (2006.01) ***C22C 38/42*** (2006.01)
C22C 38/44 (2006.01) ***C22C 38/46*** (2006.01)
C22C 38/48 (2006.01) ***C22C 38/50*** (2006.01)
C22C 38/54 (2006.01)

(86) International application number:
PCT/JP2015/006001

(87) International publication number:
WO 2016/113794 (21.07.2016 Gazette 2016/29)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **15.01.2015 JP 2015005631**

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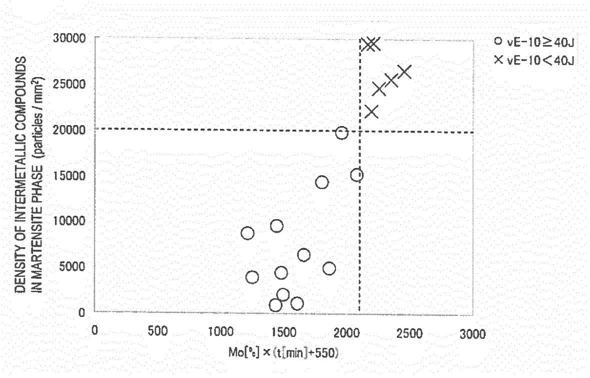
(54) **SEAMLESS STAINLESS STEEL PIPE FOR OIL WELL, AND METHOD FOR MANUFACTURING SAME**

(57) Provided are a method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods with excellent hot workability, by which a seamless stainless steel pipe for Oil Country Tubular Goods having high strength of 110ksi (=758MPa) or more in terms of yield strength, high toughness of 40J or more in terms of absorption energy vE_{-10} in a Charpy impact test at a test temperature of -10°C and excellent corrosion resistance can be acquired, and a seamless stainless steel pipe for Oil Country Tubular Goods acquired by the method. A billet which has the composition containing predetermined components and in which the contents of C, Si, Mn, Cr, Mo, Ni, N, W, Cu satisfy the predetermined relationship is heated, hot working is applied to the billet thus forming a seamless steel pipe, the seamless steel pipe is cooled to a room temperature at a cooling rate of air cooling or more, thereafter, quenching is performed by heating the seamless steel pipe to a temperature of 850°C or above and, subsequently, by cooling the seamless steel pipe to a temperature of 100 °C or below at a cooling rate of air cooling or more and, subsequently, tempering is applied to the seamless steel pipe at a temperature of 700°C or below for a predetermined holding time.

[Fig. 1]



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Description

Technical Field

[0001] The present invention relates to a seamless stainless steel pipe suitably used as a pipe for Oil Country Tubular Goods, and more particularly to a seamless stainless steel pipe having excellent corrosion resistance and further having high strength and high toughness, and a method of manufacturing such a seamless stainless steel pipe stably.

Background Art

[0002] Recently, from a viewpoint of preventing the exhaustion of oil resource (that is, crude oil and a natural gas) in regions where oil drilling is easy, the development of oil fields in regions where oil drilling is difficult has been underway. However, for example, in oil fields for drilling oil resource in a layer at a large depth from a ground, it is necessary to drill wells (oil wells) to an extremely large depth. Further, in this case, the oil resource is at a high temperature. Accordingly, there has been a demand for a pipe for Oil Country Tubular Goods which has high strength and high toughness. Furthermore, in oil fields for drilling oil resource containing CO_2, Cl^- and the like, the corrosion of a pipe for Oil Country Tubular Goods is liable to progress and hence, there has been a demand for a pipe for Oil Country Tubular Goods having corrosion resistance.

[0003] As a pipe for Oil Country Tubular Goods used in such a severe environment, a seamless steel pipe made of martensitic stainless steel containing approximately 13 mass% of Cr (so-called 13Cr steel) has been practically used. Drilling of oil resource containing a large amount of Cl^- and having a high temperature exceeding 100°C has a drawback that a pipe for Oil Country Tubular Goods cannot have sufficient strength and corrosion resistance even when a seamless steel pipe made of 13Cr steel is used.

[0004] As a pipe for Oil Country Tubular Goods which can be used in a high-temperature corrosive environment, a seamless steel pipe made of two-phase stainless steel has been developed. However, in the case of two-phase stainless steel, not only that a large amount of alloy elements is added as a raw material so that a raw material cost is pushed up but also that hot workability in manufacturing steps of a seamless steel pipe is poor and hence, productivity is lowered and, as a result, there arises a drawback that a manufacturing cost of a seamless steel pipe is pushed up.

[0005] In view of the above, techniques have been under development to acquire a seamless stainless steel pipe which can be manufactured easily and stably through a series of steps using a piercing mill adopting a skew rolling process, a general manufacturing technique of a seamless steel pipe, and which exhibits excellent corrosion resistance even at a high temperature, also having both high strength and high toughness.

[0006] For example, patent literature 1 discloses a technique where a seamless steel pipe is formed by hot working using a billet containing predetermined components, and quenching and tempering are applied to the seamless steel pipe thus acquiring a seamless stainless steel pipe which exhibits excellent corrosion resistance and has both high strength and high toughness. In this technique, however, a holding time in tempering is not taken into account. Since strength and toughness of a seamless stainless steel pipe changes corresponding to a holding time, a room for improvement still remains in such a technique from a viewpoint of the stable acquisition of desired strength.

[0007] Patent literature 2 discloses a technique where a seamless steel pipe is formed by hot working with a predetermined rolling reduction using a billet containing predetermined components, and quenching and tempering are applied to the seamless steel pipe thus acquiring a seamless stainless steel pipe which exhibits excellent corrosion resistance and has both high strength and high toughness. In this technique, however, a cooling stop temperature in quenching is not taken into account. Since strength of a seamless stainless steel pipe changes corresponding to a cooling stop temperature, a room for improvement still remains in such a technique from a viewpoint of the stable acquisition of desired strength.

Citation List

Patent Literature

[0008]

PTL 1: JP-A-2005-336595
PTL 2: JP-A-2013-249516

Summary of Invention

Technical Problem

[0009] It is an object of the present invention to overcome the drawbacks of the related art and to provide a method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods with excellent hot workability by which a seamless stainless steel pipe for Oil Country Tubular Goods which has high strength of 110ksi (=758MPa) or more in terms of yield strength, high toughness of 40J or more in terms of absorption energy vE_{-10} in a Charpy impact test at a test temperature of -10°C, and excellent corrosion resistance can be acquired , and a seamless stainless steel pipe for Oil Country Tubular Goods acquired by the method. Excellent corrosion resistance means that the seamless stainless steel pipe for Oil Country Tubular Goods exhibits corrosion resistance even at a high temperature of 230°C or above in a corrosive environment containing CO_2 and Cl^-.

Solution to Problem

[0010] Inventors of the present invention have studied an influence of quenching and tempering on toughness of a seamless stainless steel pipe. As a result, the inventors have found that the deterioration of toughness of the seamless stainless steel pipe is liable to be generated when the seamless stainless steel pipe contains a large amount of Mo and a holding time in tempering is excessively long. Based on such finding, the inventors have investigated the microstructure of a seamless stainless steel pipe which has the large content of Mo and whose toughness is deteriorated by tempering carried out for a long time and the inventors have found that a large number of intermetallic compounds are precipitated in a martensite phase. This phenomenon means that a martensite phase is formed by quenching and, thereafter, intermetallic compounds are precipitated by tempering.

[0011] Next, intermetallic compounds precipitated in a martensite phase were investigated in detail. As a result, the following findings were obtained with respect to intermetallic compounds.

(a) Mo of high concentration is present in an intermetallic compounds.
(b) A particle diameter of intermetallic compounds largely influence toughness of a seamless stainless steel pipe.
(c) It is desirable that the number of intermetallic compounds (hereinafter referred to as "density") per a unit area (mm^2) be small, and the density changes depending on a parameter P (Mo, t) =[%Mo]$\times$(t+550) calculated using the content of Mo [%Mo] (mass%) in a seamless stainless steel pipe and a holding time t (min) of tempering (see Fig. 1).

[0012] That is, to acquire a seamless stainless steel pipe for Oil Country Tubular Goods having desired strength, toughness and corrosion resistance by overcoming the problems to be solved by the present invention, it is necessary to suppress density of intermetallic compounds having a particle diameter of 0.5μm or more to $2\times10^4/mm^2$ or less, the intermetallic compounds being present in a martensite phase. Also to acquire the microstructure, it is necessary to adjust the content of Mo [%Mo] of a seamless stainless steel pipe for Oil Country Tubular Goods and a holding time t of tempering such that a parameter P(Mo, t) calculated using the content of Mo [%Mo] in a seamless stainless steel pipe for Oil Country Tubular Goods and a holding time t of tempering becomes 2100 or less. Further, to manufacture the seamless stainless steel pipe for Oil Country Tubular Goods stably, it is necessary to perform designing of composition for improving hot workability.

[0013] The present invention has been made based on such findings.

[0014] That is, a method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods according to the present invention is a method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods in which a billet having a composition which contains, by mass%, 0.005 to 0.06% C, 0.05 to 0.5% Si, 0.2 to 1.8% Mn, 0.03% or less P, 0.005% or less S, 15.5 to 18.0% Cr, 1.0 to 3.5% Mo, 1.5 to 5.0% Ni, 0.02 to 0.2% V, 0.002 to 0.05% Al, 0.01 to 0.15% N and 0.006% or less O, and further contains one or two kinds of elements selected from a group consisting of 0.5 to 3.0% W and 0.5 to 3.5% Cu such that the contents of above-described C, Si, Mn, Cr, Mo, Ni, N, W and Cu satisfy following formulae (1) and (2), and Fe and unavoidable impurities as a balance is heated, the billet is formed into a seamless steel pipe by applying hot working to the billet, the seamless steel pipe is cooled to a room temperature at a cooling rate of air cooling or more, thereafter, quenching is performed by heating the seamless steel pipe to a temperature of 850°C or above and, subsequently, by cooling the seamless steel pipe to a temperature of 100 °C or below at a cooling rate of air cooling or more and, subsequently, tempering is applied to the seamless steel pipe at a temperature of 700°C or below for a holding time which satisfies a following formula (3).

$$[\%Cr]+0.65[\%Ni]+0.6[\%Mo]+0.3[\%W]+0.55[\%Cu]-20[\%C]\geq 19.5 \cdots (1)$$

$$[\%Cr]+[\%Mo]+0.5[\%W]+0.3[\%Si]-43.5[\%C]-0.4[\%Mn]-[\%Ni]-0.3[\%Cu]-9[\%N]\geq 11.5 \cdots (2)$$

$$[\%Mo]\times(t+550)\leq 2100 \cdots (3)$$

[%C], [%Si], [%Mn], [%Cr], [%Mo], [%Ni], [%N], [%W], [%Cu]: contents (mass%) of respective elements, the content of the element being expressed as zero when the element is not contained.
t: holding time (min) of tempering

[0015] In the method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods according to the present invention, it is preferable that the billet contain, in addition to the above-mentioned composition, by mass%, one or two kinds or more of elements selected from a group consisting of 0.2% or less Nb, 0.3% or less Ti, 0.2% or less Zr and 0.01% or less B. It is preferable that the billet further contain, by mass%, 0.01% or less Ca.

[0016] A seamless stainless steel pipe for Oil Country Tubular Goods according to the present invention is a seamless stainless steel pipe for Oil Country Tubular Goods having a composition which contains, by mass%, 0.005 to 0.06% C, 0.05 to 0.5% Si, 0.2 to 1.8% Mn, 0.03% or less P, 0.005% or less S, 15.5 to 18.0% Cr, 1.0 to 3.5% Mo, 1.5 to 5.0% Ni, 0.02 to 0.2% V, 0.002 to 0.05% Al, 0.01 to 0.15% N and 0.006% or less O, and further contains one or two kinds of elements selected from a group consisting of 0.5 to 3.0% W and 0.5 to 3.5% Cu such that the contents of C, Si, Mn, Cr, Mo, Ni, N, W and Cu satisfy following formulae (1), (2), and Fe and unavoidable impurities as a balance, wherein the steel pipe has a microstructure formed of 10 to 60 volume% of ferrite phase, 0 to 20 volume% of austenite phase and a remaining portion formed of a martensite phase, and density of intermetallic compounds being present in the martensite phase and having a particle diameter of 0.5μm or more is $2\times10^4/mm^2$ or less.

$$[\%Cr]+0.65[\%Ni]+0.6[\%Mo]+0.3[\%W]+0.55[\%Cu]-20[\%C]\geq 19.5 \cdots (1)$$

$$[\%Cr]+[\%Mo]+0.5[\%W]+0.3[\%Si]-43.5[\%C]-0.4[\%Mn]-[\%Ni]-0.3[\%Cu]-9[\%N]\geq 11.5 \cdots (2)$$

[%C], [%Si], [%Mn], [%Cr], [%Mo], [%Ni], [%N], [%W], [%Cu]: contents (mass%) of respective elements, the content of the element being expressed as zero when the element is not contained.

[0017] In the seamless stainless steel pipe for Oil Country Tubular Goods according to the present invention, it is preferable that the steel pipe contain, in addition to the above-mentioned composition, by mass%, one or two kinds or more of elements selected from a group consisting of 0.2% or less Nb, 0.3% or less Ti, 0.2% or less Zr and 0.01% or less B. It is preferable that the steel pipe further contain, by mass%, 0.01% or less Ca.

Advantageous Effects of Invention

[0018] According to the present invention, it is possible to acquire stably a seamless stainless steel pipe for Oil Country Tubular Goods having both of high strength and high toughness and also having excellent corrosion resistance by the manufacturing method excellent in hot workability, and therefore a remarkable effect in industry is exerted.

Brief Description of Drawings

[0019] [Fig. 1] Fig. 1 is a graph showing the relationship between P (Mo, t) (=[%Mo]×(t+550)) and density of intermetallic compounds.

Mode for carrying out the Invention

[0020] Firstly, the composition of a seamless stainless steel pipe for Oil Country Tubular Goods according to the present invention is explained. In general, a seamless steel pipe is manufactured by applying hot working to a billet. Accordingly, the composition of the seamless stainless steel pipe for Oil Country Tubular Goods according to the present invention is equal to the composition of a billet which is a raw material for the seamless stainless steel pipe for Oil Country Tubular Goods. Hereinafter, "mass%" in the composition is simply referred to as "%".

C: 0.005 to 0.06%

[0021] C is an element having an action of increasing strength of a seamless stainless steel pipe for Oil Country Tubular Goods. When the content of C is less than 0.005%, the effect of such an action cannot be acquired. On the other hand, when the content of C exceeds 0.06%, corrosion resistance is remarkably deteriorated. Accordingly, the content of C is set to a value which falls within a range of 0.005 to 0.06%. The content of C is preferably set to a value which falls within a range of 0.01 to 0.04%.

Si: 0.05 to 0.5%

[0022] Si is an element which functions as a deoxidizing agent in the process of making molten steel for a raw material of the seamless stainless steel pipe for Oil Country Tubular Goods. When the content of Si is less than 0.05%, the effect of such a deoxidizing agent cannot be acquired. On the other hand, when the content of Si exceeds 0.5%, not only that corrosion due to CO_2 is liable to progress, but also that hot workability in the manufacturing process of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Accordingly, the content of Si is set to a value which falls within a range of 0.05 to 0.5%. The content of Si is preferably set to a value which falls within a range of 0.1 to 0.4%.

Mn: 0.2 to 1.8%

[0023] Mn is an element having an action of increasing strength of the seamless stainless steel pipe for Oil Country Tubular Goods. When the content of Mn is less than 0.2%, a desired strength cannot be acquired. On the other hand, when the content of Mn exceeds 1.8%, toughness is deteriorated. Accordingly, the content of Mn is set to a value which falls within a range of 0.2 to 1.8%. The content of Mn is preferably set to a value which falls within a range of 0.2 to 0.8%. The content of Mn is more preferably set to a value which falls within a range of 0.2 to 0.40%.

P: 0.03% or less

[0024] P is an element which deteriorates corrosion resistance of the seamless stainless steel pipe for Oil Country Tubular Goods. When the content of P exceeds 0.03%, corrosion resistance is remarkably deteriorated. Accordingly, the content of P is set to 0.03% or less. However, to decrease the content of P to less than 0.005%, it takes a long time for dephosphorization treatment in the process of making molten steel, which causes pushing up of a manufacturing cost of the seamless stainless steel pipe for Oil Country Tubular Goods. Accordingly, the content of P is preferably set to 0.005% or more.

S: 0.005% or less

[0025] S is an element which deteriorates hot workability in the manufacturing process of the seamless stainless steel pipe for Oil Country Tubular Goods. When the content of S exceeds 0.005%, the manufacture of the seamless stainless steel pipe for Oil Country Tubular Goods is obstructed. Accordingly, the content of S is set to 0.005% or less. However, in order to decrease the content of S to less than 0.0005%, it takes a long time for desulfurization treatment in the process of making molten steel, which causes pushing up of a manufacturing cost of the seamless stainless steel pipe for Oil Country Tubular Goods. Accordingly, the content of S is preferably set to 0.0005% or more.

Cr: 15.5 to 18.0%

[0026] Cr is an element having an action of improving corrosion resistance of the seamless stainless steel pipe for Oil Country Tubular Goods and particularly contributes to the prevention of corrosion caused by CO_2 in a high temperature environment. When the content of Cr is less than 15.5%, the effect of such an action cannot be acquired. On the other hand, when the content of Cr exceeds 18.0%, hot workability in the manufacturing process of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Further, when the content of Cr exceeds 18.0%, strength of the seamless stainless steel pipe for Oil Country Tubular Goods is lowered. Accordingly, the content of Cr is set to a value which falls within a range of 15.5 to 18.0%. The content of Cr is preferably set to a value which falls within a range of 16.0 to 17.5%. The content of Cr is more preferably set to a value which falls within a range of 16.5 to 17.0%.

Mo: 1.0 to 3.5%

[0027] Mo is an element having an action of improving corrosion resistance of the seamless stainless steel pipe for Oil Country Tubular Goods and particularly contributes to the prevention of pitting corrosion caused by Cl^-. When the content of Mo is less than 1.0%, the effect of such an action cannot be acquired. On the other hand, when the content of Mo exceeds 3.5%, strength is lowered. Further, when the content of Mo exceeds 3.5%, toughness is deteriorated. Still further, when the content of Mo exceeds 3.5%, a manufacturing cost of the seamless stainless steel pipe for Oil Country Tubular Goods is pushed up. Accordingly, the content of Mo is set to a value which falls within a range of 1.0 to 3.5%. The content of Mo is preferably set to a value which falls within a range of 1.5 to 3.0%. The content of Mo is more preferably set to a value which falls within a range of 2.0 to 3.0%.

[0028] Even in the case where the content of Mo falls within the above-mentioned range, when a holding time in tempering is long, intermetallic compounds are precipitated in a martensite phase and hence, toughness of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Therefore, the content of Mo [%Mo] of the seamless stainless steel pipe for Oil Country Tubular Goods and a holding time t of tempering are adjusted such that a parameter P (Mo, t)(=[%Mo]×(t+550)) satisfies the following formula (3).

$$[\%Mo]\times(t+550) \leq 2100 \cdots (3)$$

[%Mo]: content (mass%) of Mo
t: holding time (min) of tempering

Ni: 1.5 to 5.0%

[0029] Ni is an element having an action of improving corrosion resistance of the seamless stainless steel pipe for Oil Country Tubular Goods and an action of increasing strength thereof. When the content of Ni is less than 1.5%, the effect of such actions cannot be acquired. On the other hand, when the content of Ni exceeds 5.0%, a martensite phase is minimally generated and hence, strength of the seamless stainless steel pipe for Oil Country Tubular Goods is lowered. Accordingly, the content of Ni is set to a value which falls within a range of 1.5 to 5.0%. The content of Ni is preferably set to a value which falls within a range of 3.0 to 4.5%. The content of Ni is more preferably set to a value which falls within a range of 3.0 to 4.0%.

V: 0.02 to 0.2%

[0030] V is an element having an action of improving corrosion resistance of the seamless stainless steel pipe for Oil Country Tubular Goods and an action of increasing strength thereof. When the content of V is less than 0.02mass%, the effect of such actions cannot be acquired. On the other hand, when the content of V exceeds 0.2mass%, toughness is deteriorated. Accordingly, the content of V is set to a value which falls within a range of 0.02 to 0.2%. The content of V is preferably set to a value which falls within a range of 0.03 to 0.08%.

Al: 0.002 to 0.05%

[0031] Al is an element which functions as a deoxidizing agent in the process of making molten steel for a raw material of the seamless stainless steel pipe for Oil Country Tubular Goods. When the content of Al is less than 0.002%, the effect of such a deoxidizing cannot be acquired. On the other hand, when the content of Al exceeds 0.05%, alumina inclusion is liable to be precipitated and hence, hot workability in the manufacturing process of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Further, when the content of Al exceeds 0.05%, toughness is deteriorated. Accordingly, the content of Al is set to a value which falls within a range of 0.002 to 0.05%. The content of Al is preferably set to a value which falls within a range of 0.01 to 0.04%.

N: 0.01 to 0.15%

[0032] N is an element having an action of improving corrosion resistance of the seamless stainless steel pipe for Oil

Country Tubular Goods. When the content of N is less than 0.01%, the effect such an action cannot be acquired. On the other hand, when the content of N exceeds 0.15%, N combines with several kinds of elements to precipitate nitrides and hence, toughness of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Accordingly, the content of N is set to a value which falls within a range of 0.01 to 0.15%.

O: 0.006% or less

[0033] O (oxygen) is an element which is present in the seamless stainless steel pipe for Oil Country Tubular Goods as an oxide and exerts an adverse effect not only on hot workability but also on toughness and corrosion resistance. When the content of O exceeds 0.006%, O causes deterioration of hot workability, deterioration of toughness and deterioration of corrosion resistance. Accordingly, the content of O is set to 0.006% or less. The content of O is preferably set to 0.005% or less.

[0034] One or two kinds selected from a group consisting of W: 0.5 to 3.0% and Cu: 0.5 to 3.5%

[0035] In the same manner as Mo, W is an element having an action of improving corrosion resistance of the seamless stainless steel pipe for Oil Country Tubular Goods and particularly contributes to the prevention of pitting corrosion caused by Cl^-. However, when the content of W exceeds 3.0%, toughness of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Accordingly, in the case where the seamless stainless steel pipe for Oil Country Tubular Goods contains W, the content of W is set to 3.0% or less. On the other hand, also in the case where the seamless stainless steel pipe for Oil Country Tubular Goods contains W, when the content of W is less than 0.5%, a corrosion resistance improving effect cannot be acquired and hence, the content of W is set to 0.5% or more. Consequently, the content of W is set to a value which falls within a range of 0.5 to 3.0%. The content of W is preferably set to a value which falls within a range of 0.5 to 2.5%. The content of W is more preferably set to a value which falls within a range of 0.5 to 1.0%.

[0036] Cu is an element having an action of suppressing intrusion of hydrogen into the seamless stainless steel pipe for Oil Country Tubular Goods and contributes to the improvement of corrosion resistance. However, when the content of Cu exceeds 3.5%, hot workability in the manufacturing process of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Accordingly, in the case where the seamless stainless steel pipe for Oil Country Tubular Goods contains Cu, the content of Cu is set to 3.5% or less. On the other hand, also in the case where the seamless stainless steel pipe for Oil Country Tubular Goods contains Cu, when the content of Cu is less than 0.5%, a corrosion resistance improving effect cannot be acquired and hence, the content of Cu is set to 0.5% or more. Consequently, the content of Cu is set to a value which falls within a range of 0.5 to 3.5%. The content of Cu is preferably set to a value which falls within a range of 0.5 to 2.5%. The content of Cu is more preferably set to a value which falls within a range of 0.5 to 1.0%.

[0037] The contents of the respective elements C, Si, Mn, Cr, Mo, Ni, N, W and Cu are adjusted within the above-mentioned ranges such that the following formulae (1) and (2) are satisfied. In the formulae (1) and (2), [%C], [%Si], [%Mn], [%Cr], [%Mo], [%Ni], [%N], [%W] and [%Cu] indicate the contents (mass%) of the respective elements, and the content of the element is expressed as zero when the element is not contained.

$$[\%Cr]+0.65[\%Ni]+0.6[\%Mo]+0.3[\%W]+0.55[\%Cu]-20[\%C]\geq 19.5 \cdots (1)$$

$$[\%Cr]+[\%Mo]+0.5[\%W]+0.3[\%Si]-43.5[\%C]-0.4[\%Mn]-[\%Ni]-0.3[\%Cu]-9[\%N]\geq 11.5 \cdots (2)$$

[0038] By setting the contents of Cr, Ni, Mo, W, Cu and C such that the contents satisfy the formula (1) (by setting a value of the left side of the formula (1) to 19.5 or more), even in a corrosive environment which contains CO_2 and Cl^- and is besides at a high temperature (up to 230°C at maximum), a seamless stainless steel pipe for Oil Country Tubular Goods having sufficient corrosion resistance can be acquired. From a viewpoint of achieving the further improvement of corrosion resistance, it is preferable that the value of the left side of the above-mentioned formula (1) be 20.0 or more.

[0039] Further, by setting the contents of Cr, Mo, W, Si, C, Mn, Ni, Cu and N such that the contents satisfy the formula (2) (by setting a value of the left side of the formula (2) to 11.5 or more), in manufacturing steps of the seamless stainless steel pipe for Oil Country Tubular Goods, sufficient hot workability can be acquired. From a viewpoint of achieving the further improvement of hot workability, it is preferable that the value of the left side of the above-mentioned formula (2) be 12.5 or more.

[0040] The balance other than the above-mentioned component is formed of Fe and unavoidable impurities.

[0041] In addition to these elements, the seamless stainless steel pipe for Oil Country Tubular Goods may contain one or two kinds or more of elements selected from a group consisting of 0.2% or less Nb, 0.3% or less Ti, 0.2% or less Zr and 0.01% or less B.

[0042] All of Nb, Ti, Zr and B are elements having an action of increasing strength of the seamless stainless steel pipe for Oil Country Tubular Goods, and may be added when necessary. However, when the contents of these elements are excessively large, toughness of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Accordingly, the seamless stainless steel pipe for Oil Country Tubular Goods preferably contains 0.2% or less Nb, 0.3% or less Ti, 0.2% or less Zr and 0.01% or less B. On the other hand, when the contents of these elements are excessively small, the seamless stainless steel pipe for Oil Country Tubular Goods cannot acquire a strength increasing effect. Accordingly, the seamless stainless steel pipe for Oil Country Tubular Goods more preferably contains 0.02% or more Nb, 0.04% or more Ti, 0.02% or more Zr and 0.001% or more B.

Ca: 0.01mass% or less

[0043] Ca is an element having an action of spheroidizing sulfide-based inclusions. By spheroidizing sulfide-based inclusions, lattice strain around the spheroidized sulfide-based inclusions becomes small and hence, Ca suppress trapping of H and hence, Ca contributes to the improvement of corrosion resistance of the seamless stainless steel pipe for Oil Country Tubular Goods. However, when the content of Ca exceeds 0.01%, oxide-based inclusions are increased and hence, corrosion resistance is deteriorated. Accordingly, the content of Ca is preferably set to 0.01% or less. On the other hand, when the content of Ca is less than 0.0005%, a corrosion resistance improving effect cannot be acquired. Consequently, the content of Ca is more preferably set to a value which falls within a range of 0.0005 to 0.01%.

[0044] Next, steps of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods are described.

[0045] A means for making molten steel which is a raw material for a seamless stainless steel pipe for Oil Country Tubular Goods is not particularly limited, and a usual technique (for example, a converter, an electric furnace or the like) is used. Further, degassing treatment may be applied when necessary.

[0046] After making molten steel containing the components described previously, the molten steel is cast into an ingot or a slab by a usual technique (for example, continuous casting, ingot making or the like) and is formed into a billet. The billet is used as a raw material for a seamless stainless steel pipe for Oil Country Tubular Goods.

[0047] In steps of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods from a billet, the billet is subjected to conventionally known hot working (for example, hot rolling of a Mannesmann-plug mill type, hot rolling of a Mannesmann-mandrel mill type or the like) and, thereafter, is cooled to a room temperature at a cooling rate of air cooling or more thus acquiring a seamless stainless steel pipe for Oil Country Tubular Goods. Cooling at a cooling rate of air cooling or more means forced cooling (for example, immersing, injection or the like) using a refrigerant (for example, cooling water or the like) or air cooling. A cooling rate of air cooling or more indicates a cooling rate of 0.1°C/s or more. A room temperature indicates a temperature which falls within a range of 0 to 40°C.

[0048] When a heated temperature of a billet prior to hot working is excessively low, deformation resistance of the billet is increased and hence, there may be a case where an excessively large load is applied to a piercing mill (for example, a piercer mill or the like) thus causing a facility defect. On the other hand, when the heating temperature is excessively high, crystal grains of the billet becomes coarse and hence, crystal grains of a seamless stainless steel pipe for Oil Country Tubular Goods acquired through subsequent steps also becomes coarse thus deteriorating toughness of the seamless stainless steel pipe for Oil Country Tubular Goods. Further, a scale loss is increased and hence, a yield rate is lowered. Accordingly, it is preferable that a heating temperature of the billet be set to a value which falls within a range of 1100 to 1300°C. It is more preferable that the heating temperature of the billet be set to a value which falls within a range of 1200 to 1280°C.

[0049] Hot working including piercing rolling is applied to the billet heated as described above. With respect to such hot working, the present invention is applicable to, for example, hot rolling of a Mannesmann-plug mill type which can acquire a seamless stainless steel pipe for Oil Country Tubular Goods through a piercer mill, then an elongater mill, a plug mill, a reeler mill and a sizing mill or hot rolling of a Mannesmann-mandrel mill type which can acquire a seamless stainless steel pipe for Oil Country Tubular Goods through a piercer mill, mandrel mill and a reducer mill.

[0050] The seamless stainless steel pipe for Oil Country Tubular Goods acquired by hot working is readily cooled to a room temperature at a cooling rate of air cooling or more. As a result, a martensite phase is formed in the seamless stainless steel pipe for Oil Country Tubular Goods. The cooling rate of air cooling or more indicates a cooling rate of 0.1°C/s or more. The room temperature indicates a temperature which falls within a range of 0 to 90°C.

[0051] Quenching is applied to the seamless stainless steel pipe for Oil Country Tubular Goods cooled to a room temperature so that the martensite phase is further increased.

[0052] When a heating temperature prior to quenching (hereinafter referred to as a quenching temperature) is excessively low, a martensite phase is not sufficiently generated and hence, the seamless stainless steel pipe for Oil Country Tubular Goods having desired strength cannot be acquired. Accordingly, the quenching temperature is set to 850°C or above. On the other hand, when the quenching temperature is excessively high, a martensite phase is excessively formed and hence, there may be a case where the seamless stainless steel pipe for Oil Country Tubular Goods having desired toughness cannot be acquired. Consequently, it is preferable that the quenching temperature be set to a value which falls within a range of 850 to 1000°C. It is more preferable that the quenching temperature be set to a value which falls within a range of 920 to 980°C. When a holding time at this quenching temperature is excessively short, fraction ratios do not reach an equilibrium and hence, there may be a case where the seamless stainless steel pipe for Oil Country Tubular Goods cannot acquire a uniform microstructure. On the other hand, when the holding time is excessively long, the microstructure becomes coarse and hence, there may be a case where toughness is deteriorated. Accordingly, it is preferable to set the holding time to a value which falls within a range from 10 to 120 minutes.

[0053] Then, quenching is performed by cooling the seamless stainless steel pipe for Oil Country Tubular Goods heated to a predetermined quenching temperature to a temperature of 100°C or below at a cooling rate of air cooling or more. When a temperature at which quenching is stopped is more than 100°C, an austenite phase is not sufficiently transformed into a martensite phase and hence, the seamless stainless steel pipe for Oil Country Tubular Goods cannot acquire desired strength. Accordingly, such a quenching stop temperature is not desirable. The cooling rate of air cooling or more indicates a cooling rate of 0.1°C/s or more.

[0054] After quenching is completed, tempering is applied to the seamless stainless steel pipe for Oil Country Tubular Goods. When a heating temperature in tempering (hereinafter referred to as tempering temperature) is excessively high, intermetallic compounds are liable to be precipitated in a martensite phase so that toughness of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated. Accordingly, the tempering temperature is set to 700°C or below. On the other hand, when the tempering temperature is excessively low, toughness deteriorated by quenching is not sufficiently restored. Consequently, it is preferable that the tempering temperature be set to a value which falls within a range of 400 to 700°C

[0055] With respect to a holding time during which the seamless stainless steel pipe for Oil Country Tubular Goods is held at a predetermined tempering temperature in tempering, it is necessary to set the holding time such that the following formula (3) is satisfied. Unless the formula (3) is satisfied, toughness of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated.

$$[\%Mo] \times (t+550) \leq 2100 \cdots (3)$$

[%Mo]: content (mass%) of Mo
t: holding time (min) in tempering

[0056] When a predetermined holding time elapses, it is preferable to cool the seamless stainless steel pipe for Oil Country Tubular Goods to a room temperature. Such cooling may preferably be air cooling. Alternatively, the seamless stainless steel pipe for Oil Country Tubular Goods may be forcibly cooled (for example, immersing, injection or the like) using a refrigerant (for example, cooling water or the like). The room temperature indicates a temperature which falls within a range of 0 to 40°C.

[0057] The seamless stainless steel pipe for Oil Country Tubular Goods manufactured in this manner has the above-mentioned composition and, at the same time, has the microstructure formed of 10 to 60 volume% of ferrite phase, 0 to 20 volume% of austenite phase, and a remaining portion being martensite phase. When the fraction of the ferrite phase is less than 10 volume%, hot workability of the seamless stainless steel pipe for Oil Country Tubular Goods is deteriorated, while when the fraction of the ferrite phase exceeds 60 volume%, strength and toughness of the seamless stainless steel pipe for Oil Country Tubular Goods are deteriorated. When the fraction of austenite phase exceeds 20 volume%, the seamless stainless steel pipe for Oil Country Tubular Goods having desired strength cannot be acquired.

[0058] With respect to a method of determining the microstructure of the seamless stainless steel pipe for Oil Country Tubular Goods according to the present invention, firstly, a specimen for microstructure observation is sampled from a wall-thickness center portion of the steel pipe. A cross section in the wall thickness direction of the specimen is polished and, thereafter, is etched using a Villella etching solution (prepared by mixing a picric acid, a hydrochloric acid and ethanol at ratio of 2g, 10ml and 100ml, respectively), and a microstructure photograph is taken using an optical microscope (magnification: 100 to 1000 times). A martensite phase (M phase), a ferrite phase (α phase) and an austenite phase (γ phase) are determined from the microstructure photograph, and a fraction (volume ratio) of the α phase is calculated by an image analysis.

[0059] Diffracted X-ray integral intensities of a (220) plane of the γ phase and a (211) plane of the α phase are measured by an X-ray diffraction method and the fraction (volume ratio) of the γ phase is calculated using the following formula.

$$\gamma \text{ phase volume ratio } (\%) = 100/<1+\{(I\alpha \times R\gamma)/(I\gamma \times R\alpha)\}>$$

Ia : integral intensity of α phase
$I\gamma$: integral intensity of γ phase
$R\alpha$: crystallographical theoretic calculation value of α phase
$R\gamma$: crystallographical theoretic calculation value of γ phase

[0060] A fraction (volume ratio) of M phase is calculated as a balance other than those of the α phase and the γ phase.

[0061] Here, in the present invention, intermetallic compounds having a particle diameter of 0.5μm or more are precipitated and present in the martensite phase at density of $2\times10^4/mm^2$ or less. By suppressing the precipitation of intermetallic compounds in this manner, it is possible to acquire a seamless stainless steel pipe for Oil Country Tubular Goods having desired strength, toughness and corrosion resistance. Further, the billet used as a raw material for manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods also has the composition designed so as to improve hot workability and hence, it is possible to stably acquire a seamless stainless steel pipe for Oil Country Tubular Goods.

[0062] In a method of measuring the number of intermetallic compounds, firstly, the microstructure photographs of the specimens which are etched using a Villella etching solution are taken by an optical microscope (magnification: 2000 times) . Then, an equivalent circle diameter of the intermetallic compounds precipitated in a martensite phase is calculated as a particle diameter of the intermetallic compounds from the microstructure photograph, and the number of intermetallic compounds having a particle diameter of 0.5μm or more is counted.

Examples

[0063] Molten steel having the composition described in Table 1 was made, degassing being applied to the molten steel and, subsequently, a billet (100kg steel ingot) was manufactured by an ingot making method, then the billet being cooled to a room temperature (25°C). Then, the billet was heated at a temperature of 1230°C in a heating furnace and, thereafter, piercing rolling was applied to the billet by an experimenting machine of a piercer. Then, the pierced billet was water-cooled by being immersed into water vessel, and thus a seamless steel pipe (outer diameter: 83.8mm (=3.3 inches), wall thickness: 12.7mm (=0.5 inches) was prepared.

[Table 1]

Steel symbol	Component composition (mass%)													
	C	Si	Mn	P	S	Cr	Mo	Ni	V	Al	N	O	W	Cu	Nb, Ti, Zr, B, Ca
B	0.018	0.24	0.64	0.02	0.001	16.1	2.48	3.55	0.040	0.03	0.068	0.0041	0.94	0.77	Nb:0.077
C	0.023	0.19	0.58	0.02	0.001	17.4	2.78	3.86	0.038	0.02	0.051	0.0018	0.70	0.02	Nb:0.031,Ti:0.066,Zr:0.079,B:0.0018
D	0.028	0.16	0.52	0.02	0.001	16.4	3.11	3.74	0.034	0.02	0.043	0.0027	0.01	0.61	Nb:0.027,B:0.0011
E	0.018	0.18	0.44	0.01	0.001	16.3	1.69	2.77	0.058	0.02	0.071	0.0039	0.79	0.04	Ti:0.051
F	0.033	0.27	0.24	0.01	0.001	16.1	1.21	4.62	0.033	0.01	0.065	0.0034	1.03	1.15	Nb:0.048
G	0.024	0.26	0.35	0.02	0.002	16.6	2.58	3.19	0.065	0.02	0.046	0.0029	0.55	0.59	-
H	0.036	0.19	0.29	0.01	0.001	16.9	2.43	3.56	0.049	0.03	0.029	0.0033	0.02	0.95	Ca:0.0024
I	0.049	0.22	0.38	0.01	0.001	16.7	2.49	3.82	0.057	0.01	0.049	0.0045	0.89	0.01	Nb:0.055, Ca:0.0017
J	0.055	0.31	0.35	0.01	0.001	16.5	2.13	3.02	0.051	0.01	0.042	0.038	0.75	0.83	Ti:0.049, B:0.0021
K	0.053	0.13	0.34	0.02	0.001	16.5	2.06	3.93	0.034	0.01	0.068	0.034	0.01	0.98	Ti:0.044, B:0.0017

• Balance other than the components described in Table 1 being Fe and unavoidable impurities

[0064] The relationship between the compositions of steels (steel symbols B to I) described in Table 1 and the following formulae (1), (2) are described in Table 2.

$$[\%Cr]+0.65[\%Ni]+0.6[\%Mo]+0.3[\%W]+0.55[\%Cu]-20[\%C]\geq 19.5 \cdots \quad (1)$$

$$[\%Cr]+[\%Mo]+0.5[\%W]+0.3[\%Si]-43.5[\%C]-0.4[\%Mn]-[\%Ni]-0.3[\%Cu]-9[\%N]\geq 11.5 \cdots \quad (2)$$

[Table 2]

Steel symbol	Presence or non-presence of satisfaction of formula (1)*		Presence or non-presence of satisfaction of formula (2)**		Remarks
	Calculated value of left side	Determination	Calculated value of left side	Determination	
B	20.24	satisfied	13.69	satisfied	present invention example
C	21.34	satisfied	15.03	satisfied	present invention example
D	20.59	satisfied	13.77	satisfied	present invention example
E	19.01	not satisfied	14.06	satisfied	comparison example
F	20.11	satisfied	10.82	not satisfied	comparison example
G	20.23	satisfied	14.57	satisfied	present invention example
H	20.48	satisfied	13.61	satisfied	present invention example
I	19.97	satisfied	13.15	satisfied	present invention example
J	19.32	not satisfied	12.92	satisfied	comparison example
K	19.77	satisfied	11.33	not satisfied	comparison example

*)[%Cr]+0.65[%Ni]+0.6[%Mo]+0.3[%W]+0.55[%Cu]-20[%C]≥19.5··· (1)
**)[%Cr]+[%Mo]+0.5[%W]+0.3[%Si]-43.5[%C]-0.4[%Mn]-[%Ni]-0.3[%Cu]-9[%N]≥11.5 ··· (2)

[0065] Inner surfaces and outer surfaces of manufactured seamless steel pipes were observed with naked eyes, and hot workability was evaluated. The results are described in Table 4. In Table 4, the evaluation "present" was given to the seamless steel pipes where a crack having a length of 5mm or more was found, and otherwise, "not present" was given.

[0066] Quenching and tempering were applied to the manufactured seamless steel pipes. Thereafter, specimens were sampled from the resultant seamless steel pipes, and the microstructure, tensile property, toughness and corrosion resistance were investigated. The investigation method is described later. Here, conditions on heating temperature, holding time, a cooling means and cooling stop temperature in quenching, conditions on heating temperature and holding time in tempering, and a calculated value of the left side of the following formula (3) relating to tempering are described in Table 3.

[Table 3]

Steel pipe No.	Steel symbol	Quenching				Tempering				Remarks
		Heating temperature (°C)	Holding time (min)	Cooling means	Cooling stop temperature (°C)	Heating temperature (°C)	Holding time (min)	Determining satisfaction of formula (3)*		
								Calculated value of left side	Determination	
5	B	920	30	water cooling	25	600	30	1438.4	satisfied	present invention example
6	B	920	30	water cooling	25	570	120	1661.6	satisfied	present invention example
7	B	920	30	water cooling	25	560	240	1959.2	satisfied	present invention example
8	B	920	30	water cooling	25	550	360	2256.8	not satisfied	comparison example
9	C	920	30	water cooling	25	600	30	1612.4	satisfied	present invention example
10	C	920	30	water cooling	25	570	120	1862.6	satisfied	present invention example
11	C	920	30	water cooling	25	560	240	2196.2	not satisfied	comparison example
12	D	960	30	water cooling	25	600	30	1803.8	satisfied	present invention example
13	D	960	30	water cooling	25	570	120	2083.7	satisfied	present invention example
14	D	960	30	water cooling	25	560	240	2456.9	not satisfied	comparison example

(continued)

Steel pipe No.	Steel symbol	Quenching				Tempering				Remarks
		Heating temperature (°C)	Holding time (min)	Cooling means	Cooling stop temperature (°C)	Heating temperature (°C)	Holding time (min)	Determining satisfaction of formula (3)*		
								Calculated value of left side	Determination	
15	E	960	30	water cooling	25	570	120	1132.3	satisfied	comparison example
16	F	960	30	water cooling	25	570	120	810.7	satisfied	comparison example
17	G	920	80	water cooling	0	600	30	1496.4	satisfied	present invention example
18	G	920	80	water cooling	0	550	360	2347.8	satisfied	comparison example
19	H	960	80	air cooling	15	590	60	1482.3	satisfied	present invention example
20	H	960	80	air cooling	15	550	360	2211.3	satisfied	comparison example
21	I	960	30	water cooling	40	600	30	1444.2	satisfied	present invention example
22	I	960	30	water cooling	40	560	320	2166.3	satisfied	comparison example
23	J	920	30	water cooling	15	590	40	1256.7	satisfied	comparison example
24	K	920	30	water cooling	15	590	40	1215.4	satisfied	comparison example

*)$[\%Mo]\times(t+550) \leq 2100$ ··· (3)

(A) Microstructure

[0067] Specimens for microstructure observation were sampled from wall thickness center portions of seamless steel pipes which had been quenched and tempered. Cross sections of the specimens in the wall thickness direction were polished and, thereafter, etched using a Villella etching solution. Then, the photographs of the microstructures were taken through an optical microscope (magnification: 100 to 1000 times). A martensite phase (hereinafter described as "M phase"), a ferrite phase (hereinafter described as "α phase"), and an austenite phase (hereinafter described as "γ phase") were determined from the photographs of the microstructures, and a fraction of the α, phase (volume ratio) was calculated by image analyzing. The results are described in Table 4.

[0068] Diffracted X-ray integral intensities of a (220) plane of the γ phase and a (211) plane of the α phase were measured by an X-ray diffraction method, and a fraction (volume ratio) of the γ phase was calculated using the following formula. The results are described in Table 4.

$$\text{volume ratio of } \gamma \text{ phase } (\%) = 100/\langle 1+\{(I\alpha \times R\gamma)/(I\gamma \times R\alpha)\}\rangle$$

$I\alpha$: integral intensity of α phase
$I\gamma$: integral intensity of γ phase
$R\alpha$: crystallographical theoretic calculation value of α phase
$R\gamma$: crystallographical theoretic calculation value of γ phase

[0069] A fraction (volume ratio) of the M phase is shown in Table 4 as a balance other than the fractions of the α phase and the γ phase.

[0070] Next, the microstructure photographs of the specimens which were etched using a Villella etching solution (reagent prepared by mixing a picric acid, a hydrochloric acid and ethanol at ratios of 2g, 10ml and 100ml respectively) were taken through an optical microscope (magnification: 2000 times). Using the microstructure photograph, the number of intermetallic compounds having a particle diameter (equivalent circle diameter) of 0.5μm or more which were precipitated in the M phase was counted. The results are described in Table 4 as the number of intermetallic compounds per unit area (mm^2).

(B) Tensile properties

[0071] API arcuate tensile test specimens were sampled from wall-thickness center portions of seamless steel pipes which had been quenched and tempered such that the tensile direction is aligned with the pipe-axis direction in accordance with the provision stipulated in API standard. The tensile test was further carried out in accordance with the provision stipulated in API standard and, as tensile properties, yield strength YS (MPa) and tensile strength TS (MPa) were measured. The results are described in Table 4. The evaluation "qualified" was given to the specimens where the yield strength YS is 758MPa or more, and the evaluation "not qualified" was given to the specimens where the yield strength YS is less than 758MPa.

(C) Toughness

[0072] In accordance with the ISO standard, V-notched specimens (thickness: 10mm) were sampled from wall-thickness center portions of seamless steel pipes which had been quenched and tempered such that the length of the specimen is taken in the circumferential direction. Then, the Charpy impact test was carried out under a test temperature of -10°C, and an absorbed energy vE_{-10} (J) was measured. The results are described in Table 4. Three specimens were used in each test, and an arithmetic mean value of absorbed energies of three specimens was shown in Table 4. The evaluation "qualified" was given to the specimens where the absorbed energy vE_{-10} was 40J or more, and the evaluation "not qualified" was given to the specimens where the absorbed energy vE_{-10} was less than 40J.

[0073] Fig. 1 shows the relationship between a parameter P (Mo, t) =[%Mo]$\times$(t+550) and density of intermetallic compounds in respective present invention examples and the comparison examples described in Table 4. As shown in Fig. 1, the relationship of [%Mo]$\times$(t+550) $\leq$2100 is established, and the specimens which have microstructures in each of which density of intermetallic compounds being precipitated in the martensite phase and having a particle diameter of 5μm or more is 2×10^4/mm^2 or less have the absorbed energy vE_{-10} of 40J or more.

(D) Corrosion resistance

[0074] Corrosion test specimens (thickness: 3mm, width: 25mm, length: 50mm) were sampled from wall-thickness center portions of seamless steel pipes to which had been quenched and tempered, and weights of the specimens were measured. The corrosion test was carried out such that the specimens were immersed for 14 days in 20 mass% of NaCl aqueous solution (solution temperature: 230°C, saturated with CO_2 gas of 3.0MPa) held in an autoclave. After the completion of the run of corrosion test, weights of the corroded specimens were measured, and reduction amounts of weight between before and after the corrosion test were calculated in terms of thickness, and corrosion speeds (mm/year) were obtained. The results are described in Table 4. The evaluation "qualified" was given to the specimens where the corrosion speed was 0.127mm/year or less, and the evaluation "not qualified" was given to the specimens where the corrosion speed exceeded 0.127mm/year.

[0075] Next, surfaces of the corroded specimens which were already subjected to the corrosion test were observed using a loupe having the magnification of 50 times, and the presence or non-presence of the occurrence of pitting corrosion was checked. The results are described in Table 4. It is determined that pitting corrosion is present when pitting corrosion having a diameter of 0.5mm or more was observed in the surface of the seamless steel pipe, and otherwise pitting corrosion is not present.

[Table 4]

Steel pipe No.	Steel symbol	Microstructure					Tensile property		Toughness	Hot workability	Corrosion resistance		Remarks
		Kind of phase*	Ratio of M (volume%)	Ratio of α (volume%)	Ratio of γ (volume%)	Density of intermetallic compounds in M phase (particles/mm^2)	Yield strength YS(MPa)	Tensile strength TS(MPa)	vE_{-10} (J)	Presence or non-presence of cracks	Corrosion rate (mm/year)	Presence or non-presence of pitting corrosion	
5	B	M+α+γ	64	23	13	796	864	988	80.9	not present	0.108	not present	present invention example
6	B	M+α+γ	61	22	17	5967	816	943	92.2	not present	0.104	not present	present invention example
7	B	M+α+γ	65	20	15	17439	790	984	46.8	not present	0.092	not present	present invention example
8	B	M+α+γ	62	26	12	24667	873	1008	31.8	not present	0.113	not present	comparison example
9	C	M+α+γ	52	35	13	1068	794	911	98.5	not present	0.064	not present	present invention example
10	C	M+α+γ	46	38	16	4935	766	926	71.3	not present	0.072	not present	present invention example
11	C	M+α+γ	43	43	14	22160	772	929	29.7	not present	0.061	not present	comparison example
12	D	M+α+γ	62	28	10	7637	799	1027	59.3	not present	0.081	not present	present invention example
13	D	M+α+γ	70	22	8	13209	882	973	54.2	not present	0.099	not present	present invention example

(continued)

Steel pipe No.	Steel symbol	Microstructure					Tensile property		Toughness	Hot workability	Corrosion resistance		Remarks
		Kind of phase*	Ratio of M (volume%)	Ratio of α (volume%)	Ratio of γ (volume%)	Density of intermetallic compounds in M phase (particles/mm^2)	Yield strength YS(MPa)	Tensile strength TS(MPa)	vE_{-10} (J)	Presence or non-presence of cracks	Corrosion rate (mm/year)	Presence or non-presence of pitting corrosion	
14	D	$M+\alpha+\gamma$	62	27	11	26571	888	1011	38.1	not present	0.089	not present	comparison example
15	E	$M+\alpha+\gamma$	60	30	10	2811	749	960	81.4	not present	0.182	present	comparison example
16	F	$M+\alpha+\gamma$	55	17	28	3028	817	952	93.9	present	0.107	not present	comparison example
17	G	$M+\alpha+\gamma$	62	21	17	1958	781	993	69.4	not present	0.063	not present	present invention example
18	G	$M+\alpha+\gamma$	61	23	16	25564	776	989	24.5	not present	0.083	not present	comparison example
19	H	$M+\alpha+\gamma$	59	28	13	4364	807	992	88.5	not present	0.069	not present	present invention example
20	H	$M+\alpha+\gamma$	57	30	13	29634	800	1006	29.5	not present	0.073	not present	comparison example
21	I	$M+\alpha+\gamma$	59	25	16	9463	862	986	93.2	not present	0.088	not present	present invention example
22	I	$M+\alpha+\gamma$	59	25	16	29463	816	982	30.5	not present	0.067	not present	comparison example
23	J	$M+\alpha+\gamma$	53	35	12	3846	799	975	62.1	not present	0.172	present	comparison example

(continued)

Steel pipe No.	Steel symbol	Microstructure					Tensile property		Toughness	Hot workability	Corrosion resistance		Remarks
		Kind of phase*	Ratio of M (volume%)	Ratio of α (volume%)	Ratio of γ (volume%)	Density of intermetallic compounds in M phase (particles/mm^2)	Yield strength YS(MPa)	Tensile strength TS(MPa)	vE_{-10} (J)	Presence or non-presence of cracks	Corrosion rate (mm/year)	Presence or non-presence of pitting corrosion	
24	K	M+α+γ	56	15	29	8646	794	1035	73.5	present	0.073	not present	comparison example

* M: martensite, α: ferrite, γ: austenite

[0076] As can be clearly understood from Table 4, it is found that all present invention examples have, although these examples are seamless steel pipes having a large wall thickness, high strength where YS is 758MPa(=110ksi) or more, high toughness where vE_{-10} is 40J or more, and excellent corrosion resistance where no pitting corrosion occurred at a corrosion rate of 0.127mm/year or less even in a high-temperature severe environment containing CO_2 and Cl^-. Further, it is found that no cracks occurred on surfaces of the present invention examples, and the present invention examples also have excellent hot workability.

[0077] To the contrary, among the comparison examples, the steel pipes No. 8, 11, 14, 18, 20, 22, which did not satisfy the above-mentioned formula (3) in tempering, exhibited vE_{-10} of less than 40J. That is, the comparison examples are inferior to the present invention examples in terms of toughness.

[0078] The composition of the steel pipe No. 15 did not satisfy the above-mentioned formula (1) and exhibited YS of less than 758MPa. Further, in the steel pipe No. 15, the corrosion rate exceeded 0.127mm/year and pitting corrosion occurred. That is, steel pipe No. 15 is inferior to the present invention examples in terms of strength and corrosion resistance.

[0079] The composition of the steel pipe No. 16 did not satisfy the above-mentioned formula (2) and cracks occurred in a surface of the steel pipe No. 16. That is, the steel pipe No. 16 is inferior to the present invention examples in terms of hot workability.

[0080] In the steel pipe No. 23 the composition of which did not satisfy the above-mentioned formula (1), the corrosion rate of the steel pipe No. 23 exceeded 0.127mm/year and pitting corrosion occurred. That is, the steel pipe No. 23 is inferior to the present invention examples in terms of corrosion resistance.

[0081] The composition of the steel pipe No. 24 did not satisfy the above-mentioned formula (2) and cracks occurred in a surface of the steel pipe No. 24. That is, the steel pipe No. 24 is inferior to the present invention examples in terms of hot workability.

Claims

1. A method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods in which a billet having a composition which contains, by mass%, 0.005 to 0.06% C, 0.05 to 0.5% Si, 0.2 to 1.8% Mn, 0.03% or less P, 0.005% or less S, 15.5 to 18.0% Cr, 1.0 to 3.5% Mo, 1.5 to 5.0% Ni, 0.02 to 0.2% V, 0.002 to 0.05% Al, 0.01 to 0.15% N and 0.006% or less O, and further contains one or two kinds of elements selected from a group consisting of 0.5 to 3.0% W and 0.5 to 3.5% Cu such that the contents of the C, Si, Mn, Cr, Mo, Ni, N, W and Cu satisfy following formulae (1) and (2), and Fe and unavoidable impurities as a balance is heated, the billet is formed into a seamless steel pipe by applying hot working to the billet, the seamless steel pipe is cooled to a room temperature at a cooling rate of air cooling or more, thereafter, quenching is performed by heating the seamless steel pipe to a temperature of 850°C or above and, subsequently, by cooling the seamless steel pipe to a temperature of 100 °C or below at a cooling rate of air cooling or more and, subsequently, tempering is applied to the seamless steel pipe at a temperature of 700°C or below for a holding time which satisfies a following formula (3).

$$[\%Cr]+0.65[\%Ni]+0.6[\%Mo]+0.3[\%W]+0.55[\%Cu]-20[\%C]\geq 19.5 \cdots (1)$$

$$[\%Cr]+[\%Mo]+0.5[\%W]+0.3[\%Si]-43.5[\%C]-0.4[\%Mn]-[\%Ni]-0.3[\%Cu]-9[\%N]\geq 11.5 \cdots (2)$$

$$[\%Mo]\times(t+550) \leq 2100 \cdots (3)$$

[%C], [%Si], [%Mn], [%Cr], [%Mo], [%Ni], [%N], [%W], [%Cu]: contents (mass%) of respective elements, the content of the element being expressed as zero when the element is not contained.
t: holding time (min) of tempering

2. The method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods according to claim 1, wherein the billet contains, in addition to the composition, by mass%, one or two kinds or more of elements selected

from a group consisting of 0.2% or less Nb, 0.3% or less Ti, 0.2% or less Zr and 0.01% or less B.

3. The method of manufacturing a seamless stainless steel pipe for Oil Country Tubular Goods according to claim 1 or 2, wherein the billet contains, in addition to the composition, by mass%, 0.01% or less Ca.

4. A seamless stainless steel pipe for Oil Country Tubular Goods having a composition which contains, by mass%, 0.005 to 0.06% C, 0. 05 to 0.5% Si, 0.2 to 1.8% Mn, 0.03% or less P, 0.005% or less S, 15.5 to 18.0% Cr, 1.0 to 3.5% Mo, 1.5 to 5.0% Ni, 0.02 to 0.2% V, 0.002 to 0.05% Al, 0.01 to 0.15% N and 0.006% or less O, and further contains one or two kinds of elements selected from a group consisting of 0.5 to 3.0% W and 0.5 to 3.5% Cu such that the contents of C, Si, Mn, Cr, Mo, Ni, N, W and Cu satisfy following formulae (1), (2), and Fe and unavoidable impurities as a balance, wherein the steel pipe has a microstructure formed of 10 to 60 volume% of a ferrite phase, 0 to 20 volume% of an austenite phase and a remaining portion formed of a martensite phase, and density of intermetallic compounds being present in the martensite phase and having a particle diameter of 0.5μm or more is $2\times10^4/mm^2$ or less.

$$[\%Cr]+0.65[\%Ni]+0.6[\%Mo]+0.3[\%W]+0.55[\%Cu]-20[\%C]\geq19.5 \cdots (1)$$

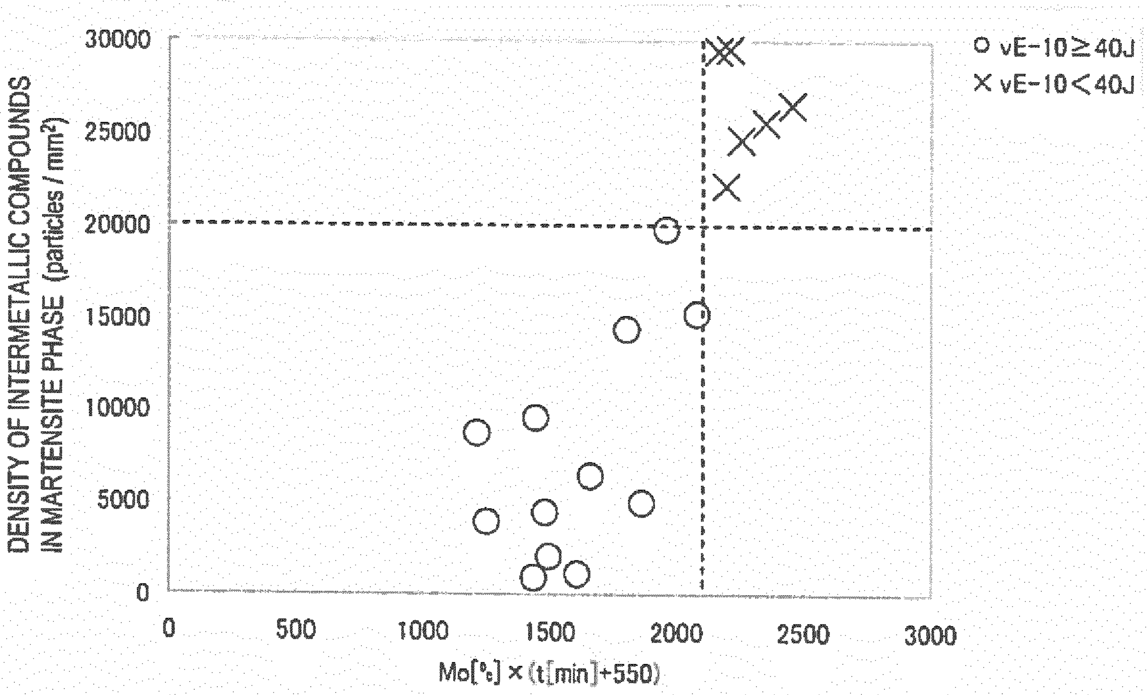
$$[\%Cr]+[\%Mo]+0.5[\%W]+0.3[\%Si]-43.5[\%C]-0.4[\%Mn]-[\%Ni]-0.3[\%Cu]-9[\%N]\geq11.5 \cdots (2)$$

[%C], [%Si], [%Mn], [%Cr], [%Mo], [%Ni], [%N], [%W], [%Cu]: contents (mass%) of respective elements, the content of the element being expressed as zero when the element is not contained.

5. The seamless stainless steel pipe for Oil Country Tubular Goods according to claim 4, wherein the seamless stainless steel pipe contains, in addition to the composition, by mass%, one or two kinds or more of elements selected from a group consisting of 0.2% or less Nb, 0.3% or less Ti, 0.2% or less Zr and 0.01% or less B.

6. The seamless stainless steel pipe for Oil Country Tubular Goods according to claim 4 or 5, wherein the seamless stainless steel pipe contains, in addition to the composition, by mass%, 0.01% or less Ca.

[Fig. 1]


30000
25000
20000
15000
10000
5000
0
DENSITY OF INTERMETALLIC COMPOUNDS IN MARTENSITE PHASE (particles / mm²)
0
500
1000
1500
2000
2500
3000
Mo[%] × (t[min]+550)
○ vE-10≧40J
× vE-10＜40J

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/006001

A. CLASSIFICATION OF SUBJECT MATTER
C21D8/10(2006.01)i, *C21D9/08*(2006.01)i, *C22C38/00*(2006.01)i, *C22C38/58*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C21D8/10, C21D9/08, C22C38/00-C22C38/60

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005-336595 A (JFE Steel Corp.), 08 December 2005 (08.12.2005), claims; 0001, 0013, 0044 to 0046, 0050 to 0054, 0058 to 0065; tables 1, 2 & US 2006/0243354 A1 0001, 0012, 0078 to 0081, 0085 to 0089, 0093 to 0105; tables 1, 1-continued, 2, 2-continued; claims & WO 2005/017222 A1 & EP 1662015 A1 & BR PI0413626-8 A & CN 1836056 A	1-6
X	JP 2008-81793 A (JFE Steel Corp.), 10 April 2008 (10.04.2008), claims; 0001, 0011 to 0012, 0032 to 0033, 0035 to 0044; tables 1, 2, 3 (Family: none)	1-6

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 February 2016 (23.02.16)	08 March 2016 (08.03.16)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/006001

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2013-249516 A (JFE Steel Corp.), 12 December 2013 (12.12.2013), claims; 0007, 0025 to 0037, 0042 to 0047, 0051; tables 1, 2, 3 & US 2015/0101711 A1 0009 to 0010, 0045 to 0066, 0074 to 0088; tables 1, 2, 2-continued, 3, 3-continued; claims & WO 2013/179667 A1 & EP 2857530 A1 & AU 2013268908 A1 & CA 2872342 A1 & CN 104379774 A	2-3,5-6 1,4
A	JP 2014-114500 A (JFE Steel Corp.), 26 June 2014 (26.06.2014), claims; 0022 & US 2015/0315667 A1 0031 to 0032; claims & WO 2014/091756 A1 & EP 2933344 A1 & CN 104854250 A	1-6
A	WO 2013/146046 A1 (Nippon Steel & Sumitomo Metal Corp.), 03 October 2013 (03.10.2013), & JP 5348354 B1 & US 2015/0047831 A1 & EP 2832881 A1 & AU 2013238482 A1 & CA 2863187 A1 & CN 104204253 A & MX 2014009444 A & AR 090306 A1	1-6
A	JP 2012-149317 A (JFE Steel Corp.), 09 August 2012 (09.08.2012), (Family: none)	1-6
A	WO 2011/136175 A1 (Sumitomo Metal Industries, Ltd.), 03 November 2011 (03.11.2011), & JP 4911266 B2 & US 2012/0328897 A1 & EP 2565287 A1 & AU 2011246246 A1 & CA 2795326 A1 & CN 102869803 A & MX 2012012435 A & RU 2012150801 A & AR 081457 A1	1-6
A	JP 2010-209402 A (JFE Steel Corp.), 24 September 2010 (24.09.2010), (Family: none)	1-6

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/006001

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	JP 2015-110822 A (JFE Steel Corp.), 18 June 2015 (18.06.2015), claims; 0001, 0011, 0026, 0043 to 0048; tables 1, 2 & US 2015/0315684 A1 0001, 0012 to 0013, 0046 to 0047, 0076 to 0086; tables 1-1, 1-1-continued, 1-2, 1-2-continued, 2-1, 2-2, 2-2-continued; claims & WO 2014/097628 A1 & EP 2918697 A1 & CN 104884658 A	1-6

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- JP 2013249516 A **[0008]**